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MORPHOLOGY OF PLUTONIUM PRECIPITATES IN THE PRESENCE OF GOETHITE AT 25 AND 80°C

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Plutonium (Pu) has been identified as a dominant long-term dose contributor under certain nuclear waste repository scenarios. The transport of Pu will likely occur by association with colloids that migrate through the engineered barrier system and host rock. We have examined the behavior of aqueous Pu(IV) and intrinsic Pu nano-colloids in the presence of goethite, across a range of concentrations that span the solubility of $\text{PuO}_{2+x}(\text{s,hyd})$, at 25 and 80°C, and after equilibration for over 100 days. The strong affinity of aqueous Pu(IV) for the goethite surface is explained by the epitaxial growth of bcc Pu_4O_7 nano-colloids on goethite. The 2-5 nm Pu_4O_7 nano-colloids are dispersed across the goethite surface and stable over the timescale of months at both 25 and 80°C. There is no indication that the Pu_4O_7 alters to a more stable PuO_2 nano-colloid. PuO_2 nano-colloids reacted with goethite have a very weak affinity for the goethite surface. Instead, bulk aggregation of PuO_2 nano-colloids is observed, with greater aggregation at 80°C compared to 25°C. From a $\text{PuO}_{2+x}(\text{s,hyd})$ solubility perspective, this would be characterized as precipitation.

I. INTRODUCTION

Plutonium (Pu) has been identified as a dominant long-term dose contributor under certain nuclear waste repository scenarios.^{1,2} Pu transport will likely occur by association with natural or anthropogenic colloids or as intrinsic colloids that migrate through the engineered barrier system and host rock.³ The dominant anthropogenic colloids may be iron oxides produced as a result of steel corrosion² or intrinsic colloids formed at relatively high actinide concentrations. The mineralogy of natural colloids will be a function of the host rock mineralogy or backfill material. At high concentrations ($>10^{-9}$ M), Pu tends to form intrinsic nano-colloids.⁴ However, it is not known whether these Pu nano-colloids initially formed at high concentrations remain stable at lower (e.g., $<10^{-9}$ M) concentrations that would be expected as the intrinsic Pu colloids move down gradient from a repository.

The structure of Pu precipitates and nano-colloids has been investigated for many years.^{5,6} Early electron microscopy studies by Haire et al.⁵ concluded that fresh Pu(IV) precipitates are composed of nanoparticles <2.5 nm in size (Fig. 1). The degree of crystallinity could be increased (based on x-ray diffraction line broadening) by “aging” the precipitates for a few hours in $<100^\circ\text{C}$ water. However, the fundamental size of these nanoparticles does not change. Importantly, these nanoparticles were found to aggregate and were not considered stable in solution. Peptization (formation of a stable dispersion of Pu colloids in water) occurred when these precipitates were heated and reacted with ~ 0.2 M HNO_3 . The colloidal products of this peptization have a Pu: NO_3 ratio of ~ 1 . Larger crystallites (4–10 nm) could be produced only upon heating (250°C or greater), which also reduced the NO_3^-/Pu ratio of the colloids from ~ 1 to ~ 0.1 .⁶

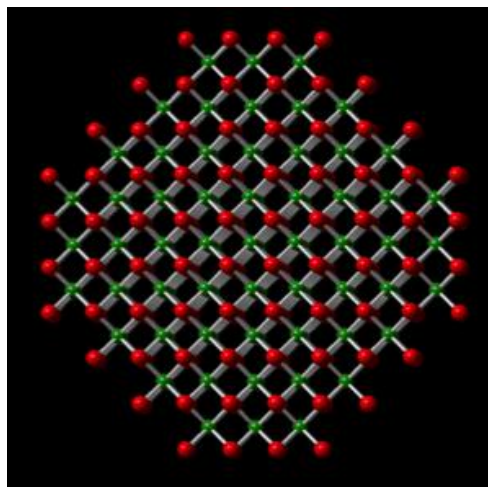


Fig. 1. Idealized structure of a 2.5 nm fcc PuO_2 nanoparticle. Each Pu(IV) atom (green) is coordinated by 8 O atoms (red).

Soderholm et al.⁷ examined the structure and formation of stable colloidal suspensions of Pu precipitates in HCl/LiCl solutions. Upon evaporation from high salt solutions (2 M LiCl), a novel precipitate was formed in

which PuO₂-like nano-clusters, “decorated” by Cl⁻ anions (Fig. 2), formed a superlattice structure. This stabilization of Pu sols in high ionic strength solutions is consistent with historical schemes developed as part of the sol-gel process. The unique scientific contribution of the Soderholm et al.⁷ work was the identification of well-ordered Pu nanoclusters that is in direct contrast to the traditional assumptions of poorly ordered polymeric or amorphous Pu(IV) precipitates. It also suggests that the <2.5 nm sols produced by Haire et al.⁵ in dilute HNO₃ with a Pu:NO₃ ratio of ~1 may be morphologically related to these nano-clusters (Pu:Cl ratio of 0.7). However, the stability relationship between these nano-clusters and larger nano-colloids produced upon aging and heating of Pu(IV) precipitates/sols has yet to be understood.

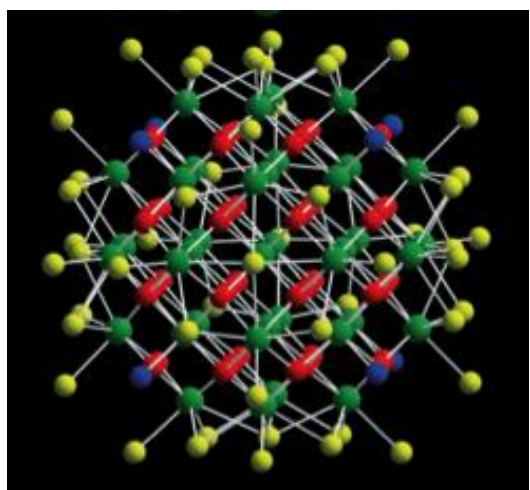


Fig. 2. Structure of Pu(IV) nano-clusters formed in LiCl solution; the PuO₂ framework exhibits a slightly distorted fcc packing of crystalline PuO₂. Each Pu(IV) atom (green) is coordinated to O (red), H₂O (blue), and/or Cl atoms that decorate the surface of the cluster (yellow). From Soderholm et al.⁷

Powell et al.⁸ examined the behavior of Pu(IV) surface precipitates and colloids in the presence of goethite and quartz. Transmission electron microscopy (TEM) was used to characterize the morphology of Pu associated with these mineral phases. Plutonium was added to goethite as aqueous Pu(IV). Plutonium nano-colloids (2-5 nm) that formed on goethite underwent a lattice distortion relative to the ideal fluorite-type structure, fcc, PuO₂, resulting in the formation of a bcc, Pu₄O₇. This structural distortion resulted from an epitaxial growth of the plutonium colloid on goethite, leading to stronger binding of plutonium compared with other minerals such as quartz where the distortion was not observed.

The results of Powell et al.⁸ and earlier studies suggest that the morphology, structure, and stability of Pu

can vary dramatically and affect the sorptivity and mobility of Pu in the environment. An understanding of the stability of Pu nano-clusters and colloids and sorption/desorption kinetics of monomeric and colloidal Pu on common minerals is critical to predicting long-term colloid-facilitated transport behavior of Pu.⁹⁻¹³

Here, we report on the sorption behavior of Pu at elevated temperatures in the presence of goethite (α-FeOOH) over a range of concentrations that span solubility-controlled to adsorption-controlled concentrations. We focus on the sorptive behavior of two common forms of Pu: aqueous Pu(IV) and intrinsic Pu(IV) nano-colloids at 25 and 80°C in a dilute pH 8 NaCl/NaHCO₃ solution. The morphology of Pu sorbed to goethite was characterized using TEM.

II. MATERIALS AND METHODS

Two series of batch sorption experiments were conducted. In the first series, aqueous Pu(IV) was reacted with goethite at 25 and 80°C. Three initial Pu concentrations were used such that the resulting equilibrium Pu concentration would be below, above, and near the PuO_{2+x}(s,hyd) solubility ($\sim 5 \times 10^{-9}$ M).⁴ The experiment was intended to test whether the affinity or morphology of sorbed Pu was temperature and/or concentration dependent. In the second set of experiments, intrinsic Pu(IV) nano-colloids were reacted with goethite at 25 and 80°C. The intrinsic Pu(IV) nano-colloid sorption experiments were intended to test whether the initial form of Pu affects its long-term sorption behavior and evaluate the stability of Pu(IV) nano-colloids as a function of temperature and concentration.

Alpha-emitting ²⁴²Pu (> 99.8% by mass) was used in the experiments. The Pu stock solution (7.6×10^{-4} M Pu(IV) in 2.06 M HCl) was purified using AG1x8 100–200 mesh anion exchange resin and filtered through a 3 kD molecular weight cut-off (MWCO) filter. The oxidation state of Pu was confirmed using both UV/Vis and solvent extraction. The aqueous Pu(IV) working solution was prepared by diluting the stock solution to 1.9×10^{-4} M Pu(IV) in 1 N HCl. The intrinsic Pu(IV) nano-colloid working solution was prepared by adding 1 mL 1N NaOH and 0.39 mL pH 8 buffer (5 mM NaCl/0.7 mM NaHCO₃) to 0.53 mL of the Pu(IV) stock. 1 N NaOH was added to gradually adjust the pH to ~8.5. The intrinsic Pu colloids were washed 3 times and re-suspended in pH 8 buffer solution. The final Pu(IV) nano-colloid concentration was 1.5×10^{-4} M. Based on TEM, the fundamental particle size of intrinsic Pu nano-colloids prepared in this manner is 2-5 nm.

Goethite was synthesized from Fe(NO₃)₃•9H₂O as described by Schwertmann and Cornell.¹⁴ Goethite was washed with a 5 mM NaCl/0.7 mM NaHCO₃ buffer solution, sonicated for 5 minutes, and centrifuged for 60

minutes at 3500 rpm three times until constant pH was reached. X-ray diffraction confirmed goethite as the major phase, the point of zero salt effect was 8.5 ± 0.1 , and the BET surface area was $16 \text{ m}^2/\text{g}$. Additional characterization data are reported elsewhere.¹⁵

All batch experiments were conducted in 10 mL Nalgene* Oak Ridge polycarbonate centrifuge tubes with sealing caps. Either aqueous Pu(IV) or intrinsic Pu(IV) nano-colloids were spiked into 9 mL of 5 mM NaCl/0.7 mM NaHCO_3 in which goethite (solid to liquid ratio of 0.1 g/L) had previously been added. For the aqueous Pu(IV) experiments, an equivalent amount of NaOH was added before adding the Pu spike to ensure a final solution pH of 8. The 10 mL tubes were submerged in 50 mL polypropylene conical centrifuge tubes filled with Milli-Q water to minimize evaporative losses and provide secondary containment to the radioactive samples. Over the course of the experiment, the 25°C sample tubes were stored vertically in a hood. The 80°C sample tubes were submerged in a heated water bath. All samples were allowed to react for 103 days. Both liquid scintillation counting (LSC) and ICP-MS were used to determine Pu concentration.

At the conclusion of each experiment, the solid phases were washed in MQ ($>18 \text{ M}\Omega$) water three times by sequentially centrifuging at 5000 rpm for 90 minutes, decanting the supernatant, and replacing it with fresh MQ water. The washing was performed to remove salts from solution. The solids were resuspended in MQ water by sonicating for 5 minutes and diluting 10 \times to produce a 0.01 g/L suspension. A volume of 2 to 5 μL of each suspension was deposited on TEM carbon-coated copper grids and dried in a glass desiccator. All analyses were performed on a Philips CM 300 FEG TEM operating at 300kV, equipped with a Gatan Imaging Filter (GIF) with a $2\text{k} \times 2\text{k}$ CCD camera and an EDX detector.

III. RESULTS AND DISCUSSION

III.A. Aqueous Pu(IV) Sorption to Goethite, 25°C

In the presence of goethite at 25°C, aqueous Pu(IV) has been shown to grow epitaxially, forming bcc Pu_4O_7 nano-colloids in the 2-5 nm particle size range.⁸ While previous observations were made on samples reacted for short durations, the Pu_4O_7 nano-colloids in this study appear to be stable over the longer experiment time frame of 103 days. Importantly, this indicates that the Pu_4O_7 is stable on the goethite surface and will not alter to a PuO_2 phase over a time frame of months.

Identification of PuO_2 versus Pu_4O_7 on the goethite surface was accomplished by high-resolution TEM imaging (HRTEM) combined with fast Fourier transform (FFT) analysis (HRTEM FFT) (data not shown). However, we have also found that the two forms exhibit distinct morphological characteristics at the nano-scale. In

general, PuO_2 nano-particles form aggregates that range in size from tens to hundreds of nanometers while Pu_4O_7 nano-colloids are uniquely associated on the goethite surface and distributed as dispersed 2-5 nm nano-particles.

In the low concentration aqueous Pu(IV) sample, formation of nano-colloids was not observed by TEM, consistent with solubility estimates.⁴ In the intermediate concentration aqueous Pu(IV) sample, Pu_4O_7 nano-colloids are widely distributed over the goethite surface and dominated by isolated (dispersed) 2-5 nm nano-colloids (Fig. 3). In the high-concentration aqueous Pu(IV) sample, both dispersed Pu_4O_7 nano-colloids and aggregated fcc PuO_2 nano-colloids exist. Importantly, the fundamental crystalline size remains in the 2-5 nm size range for both forms of Pu nano-colloid and in all samples. In the high-concentration sample, nano-colloid aggregation is more pronounced. It cannot be ascertained whether this aggregation of PuO_2 nanoparticles is purely a physical/electrostatic interaction or a chemical one. Importantly, aggregated nano-colloids appear to be dominated by PuO_2 nano-colloids precipitated directly from solution and weakly associated with the goethite surface. From a bulk solution standpoint, this consistent with precipitation of $\text{PuO}_{2+x}(\text{s,hyd})$.⁴ At the nanoscale, it appears as aggregation of PuO_2 nano-colloids.

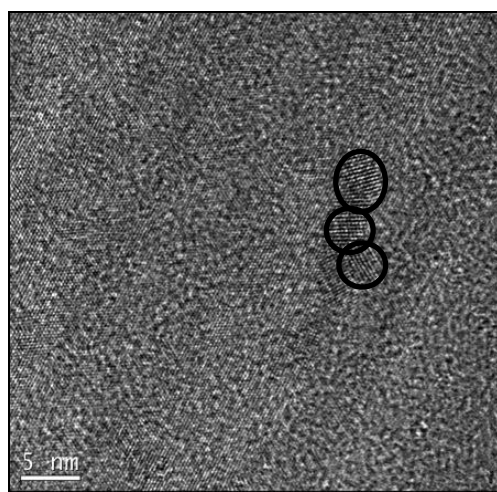


Fig. 3. Dispersed Pu_4O_7 on the goethite surface retains its 2-5 nm particle size after 3 months of equilibration at 25°C (1800 ppm Pu on goethite). Large aggregates and/or alteration to PuO_2 were not observed.

III.B. Intrinsic Pu(IV) Nano-Colloid sorption to Goethite, 25°C

Unlike aqueous Pu(IV) sorption, intrinsic Pu(IV) nano-colloid sorption to goethite is dominated by aggregated mats of PuO_2 nano-colloids (Fig. 4). These mats were observed in both the intermediate- and high-

concentration samples. The Pu_4O_7 colloids that were observed in the aqueous Pu(IV) experiments were not observed in any of the intrinsic Pu colloid experiments. This indicates that the PuO_2 colloids, once formed, will not alter to Pu_4O_7 over a timeframe of months and under these conditions.

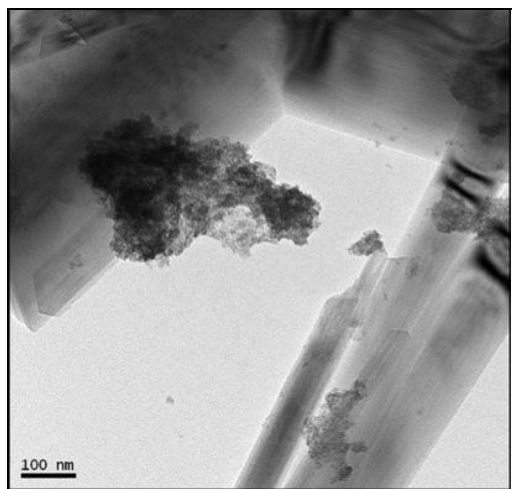


Fig. 4. At 25°C, intrinsic PuO_2 nano-colloids form aggregates at intermediate and high Pu concentrations. Pu nano-colloids that are characteristic of Pu_4O_7 surface precipitation are not present.

Because the PuO_2 nano-colloid mats are located both on and off goethite, it is clear that the interaction between intrinsic PuO_2 nano-colloids and the goethite surface is much weaker than in the case of aqueous Pu(IV) sorption. The bulk solution chemistry data suggest that the same weak interaction between PuO_2 nano-colloids and goethite exist in the low Pu concentration samples (data not shown). However, identification of PuO_2 colloids by TEM at low surface loading is exceedingly difficult. It was not attempted for the low-concentration sample.

III.C. Aqueous Pu(IV) sorption to Goethite, 80°C

The characteristics of Pu associated with goethite at 80°C are not substantially different from those at 25°C. The intermediate-concentration aqueous Pu(IV) sample is dominated by dispersed Pu_4O_7 nano-colloids that are in the 2-5 nm size range. In the high-concentration sample, both aggregated PuO_2 nano-colloids and dispersed Pu_4O_7 nano-colloids are present (Fig. 5). The aggregated PuO_2 nano-colloids are located both on and off the goethite surface while the Pu_4O_7 nano-colloids are strictly associated with the goethite surface. The Pu_4O_7 nano-colloids are formed epitaxially on the goethite surface. In contrast, PuO_2 nano-crystals most likely form from aqueous Pu in solution with minimum interaction with goethite.

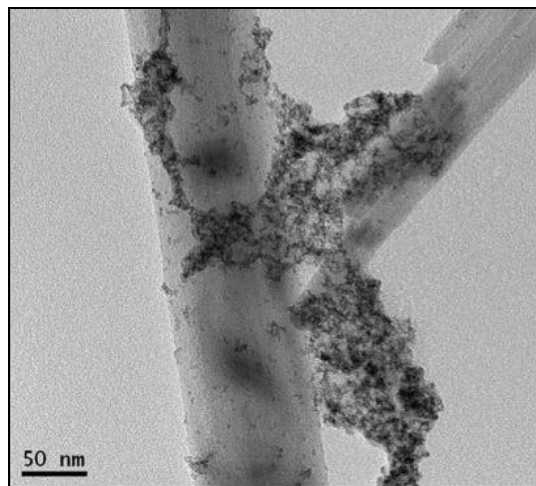


Fig. 5. At 80°C, high (8900 ppm) aqueous Pu samples that were reacted with goethite for 3 months produced a mixture of dispersed Pu_4O_7 and aggregated PuO_2 . The PuO_2 aggregates are weakly associated with the goethite surface.

III.D. Intrinsic Pu(IV) Nano-Colloid sorption to Goethite, 80°C

The behavior of intrinsic Pu(IV) nano-colloids at 80°C is dominated in both intermediate- and high-concentration samples by the formation of large aggregated PuO_2 nano-colloids and little if any association with the goethite surface (Fig. 6). In terms of

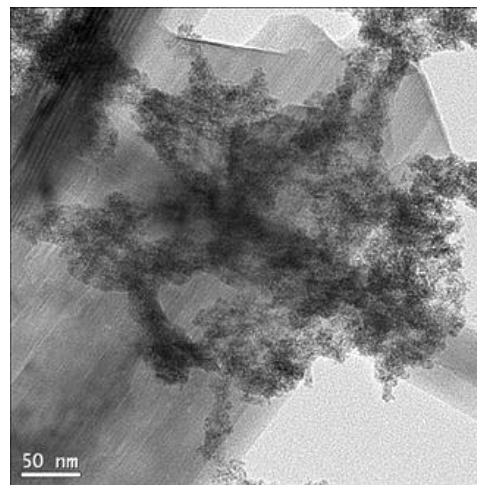


Fig. 6. At 80°C, high (10,000 ppm) concentration intrinsic PuO_2 nano-colloids reacted with goethite for 3 months produce only aggregated PuO_2 that is weakly associated with goethite. The goethite surface is devoid of dispersed Pu_4O_7 (or PuO_2) colloids in these samples.

bulk solution chemistry, these would be considered precipitates of $\text{PuO}_{2+x}(\text{s,hyd})$. HRTEM images and electron diffraction analysis indicate that the mats are composed of 2-5 nm nano-colloids with an fcc PuO_2 structure. Importantly, the results suggest that the relationship between colloidal and precipitated forms of $\text{PuO}_{2+x}(\text{s,hyd})$ is controlled by degree of aggregation of 2-5 nm nano-colloids. Aggregation of nano-colloids is likely controlled by the solution conditions in which they are present—Pu concentration, solution composition (e.g., ionic strength, pH) and temperature.

IV. CONCLUSIONS

The strong affinity of aqueous Pu(IV) for the goethite surface is explained by the epitaxial growth of bcc Pu_4O_7 nano-colloids on goethite. The behavior is affected minimally by temperature. However, the dispersed 2-5 nm Pu_4O_7 nano-colloids on the goethite surface appear to be stable over the timescale of months at both 25 and 80°C under our experimental conditions. There is no indication that the Pu_4O_7 alters to PuO_2 nano-colloids over time. When intrinsic PuO_2 nano-colloids are reacted with goethite over 103 days, both solution phase characterization in low-concentration samples and TEM of high-concentration samples indicate that the PuO_2 nano-colloids have a very weak affinity for the goethite surface. Importantly, there is no indication that the PuO_2 will alter to Pu_4O_7 nano-colloids on the goethite surface over time. Thus it appears that the association of Pu to goethite is dependent on the initial state of Pu in solution.

The crystallite size of PuO_2 nano-colloids is in the 2-5 nm range and appears to increase only slightly at higher temperatures and over time, consistent with earlier characterization of plutonium sols.⁵ Aggregation of PuO_2 nano-colloids is favored over sorption to goethite. From a bulk solubility perspective, our data are consistent with recent solubility measurements for $\text{PuO}_{2+x}(\text{s,hyd})$.⁴ However, the exact relationship between the nano-clusters of Soderholm et al.², the larger nano-colloids observed here, and solubility measurement of Neck et al.⁴ requires further study.

The fate of Pu in the environment is dependent on its initial form and its subsequent stability under changing geochemical conditions. Epitaxial growth of Pu_4O_7 on the goethite surface will produce a strong association between Pu and goethite, which could lead to its immobilization. However, the formation of Pu_4O_7 on goethite, as a colloid, has the potential to facilitate the transport of Pu.

The focus of ongoing research is on the dissolution kinetics of Pu nanoparticles and sorbed species from the iron hydroxide. Pu nanoparticle dissolution and Pu desorption kinetics must be quantified as these rates are likely to control the colloid-facilitated transport of Pu in the near-field and far-field repository environments.

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